



Selective methanation of CO over supported Ru catalysts

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ABSTRACT

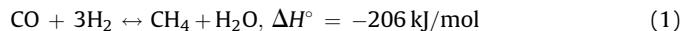
The catalytic performance of supported ruthenium catalysts for the selective methanation of CO in the presence of excess CO₂ has been investigated with respect to the loading (0.5–5.0 wt.%) and mean crystallite size (1.3–13.6 nm) of the metallic phase as well as with respect to the nature of the support (Al₂O₃, TiO₂, YSZ, CeO₂ and SiO₂). Experiments were conducted in the temperature range of 170–470 °C using a feed composition consisting of 1%CO, 50% H₂, 15% CO₂ and 0–30% H₂O (balance He). It has been found that, for all catalysts investigated, conversion of CO₂ is completely suppressed until conversion of CO reaches its maximum value. Selectivity toward methane, which is typically higher than 70%, increases with increasing temperature and becomes 100% when the CO₂ methanation reaction is initiated. Increasing metal loading results in a significant shift of the CO conversion curve toward lower temperatures, where the undesired reverse water–gas shift reaction becomes less significant. Results of kinetic measurements show that CO/CO₂ hydrogenation reactions over Ru catalysts are structure sensitive, i.e., the reaction rate per surface metal atom (turnover frequency, TOF) depends on metal crystallite size. In particular, for Ru/TiO₂ catalysts, TOFs of both CO (at 215 °C) and CO₂ (at 330 °C) increase by a factor of 40 and 25, respectively, with increasing mean crystallite size of Ru from 2.1 to 4.5 nm, which is accompanied by an increase of selectivity to methane. Qualitatively similar results were obtained from Ru catalysts supported on Al₂O₃. Experiments conducted with the use of Ru catalyst of the same metal loading (5 wt.%) and comparable crystallite size show that the nature of the metal oxide support affects significantly catalytic performance. In particular, the turnover frequency of CO is 1–2 orders of magnitude higher when Ru is supported on TiO₂, compared to YSZ or SiO₂, whereas CeO₂- and Al₂O₃-supported catalysts exhibit intermediate performance. Optimal results were obtained over the 5%Ru/TiO₂ catalyst, which is able to completely and selectively convert CO at temperatures around 230 °C. Addition of water vapor in the feed does not affect CO hydrogenation but shifts the CO₂ conversion curve toward higher temperatures, thereby further improving the performance of this catalyst for the title reaction. In addition, long-term stability tests conducted under realistic reaction conditions show that the 5%Ru/TiO₂ catalyst is very stable and, therefore, is a promising candidate for use in the selective methanation of CO for fuel cell applications.

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1. Introduction

The methanation reaction has been widely used in industry as an efficient method for the removal of carbon oxides from inlet streams in hydrogen or ammonia plants [1]. The interest for the reaction has grown significantly during the last few years as a result of recent advancements in fuel cell technology and the need for development of fuel processors capable of converting carbonaceous fuels into hydrogen [2,3]. In such systems, the CO methanation reaction (Eq. (1)) could be used as the final purification step of reformate gas to reduce concentration of CO

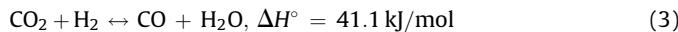
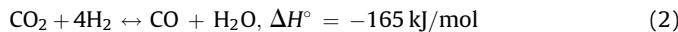
to the extremely low levels (<50 ppm) dictated by the poisoning limit of PEM fuel electrodes [4–7].



This approach offers certain advantages, compared to preferential oxidation (PROX) of CO [2,3,8,9], because it does not require addition of oxygen (air) in the hydrogen-rich gas stream, which may give rise to various problems related to reduced hydrogen yield, dilution, safety and restrictions in the operating parameters. In addition, methane produced is inert to the PEM fuel cell electrodes and can be utilized in the afterburner. However, depending on the operating conditions and catalyst employed, reaction (1) may run in parallel with the undesired methanation of CO₂, which consumes significant quantities of valuable hydrogen

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(Eq. (2)), as well as with the reverse water–gas shift (RWGS) reaction (Eq. (3)), which shifts CO₂ to CO.



Consequently, it is important to develop stable and selective CO methanation catalysts with sufficiently high activity at low temperatures, able to suppress both CO₂ methanation and RWGS reactions.

Hydrogenation of carbon oxides toward methane and higher hydrocarbons can be catalyzed by several metal catalysts, including Ni [10–15], Ru [2,10,16–21] and Rh [18,21–23]. Ruthenium catalysts dispersed on metal oxide carriers have been found to exhibit high activity for the solo-methanation of CO [2,10,16,24] or CO₂ [17–20] as well as for the co-methanation of CO/CO₂ mixtures [9,16,21,25]. For instance, Vannice [24] reported that the specific activity of Ru/Al₂O₃ for CO hydrogenation is about one order of magnitude higher, compared to that of Al₂O₃-supported Rh or Pd. Ruthenium (and also Rh and Ni) is also very active for hydrogenation of CO/CO₂ mixtures in contrast to Pt, which tends to catalyze the RWGS reaction [16,21,25]. A number of studies have shown that the nature of the support may play a crucial role in the mechanism of CO/CO₂ hydrogenation reactions, since metal–support interactions can modify the catalytic properties of the metallic phase [22,26–28]. In addition, catalytic performance of dispersed metal catalysts for methanation reactions is often affected by metal loading and crystallite size in a manner which depends on operating conditions used and metal–support combination employed [9,26,29–32].

In our recent study [21] we have investigated the effects of the nature of the metallic phase on the performance of Al₂O₃-supported Ru, Rh, Pt and Pd catalysts for the methanation of CO, CO₂ and their mixtures both in the absence and in the presence of water in the feed. It has been found that Ru and Rh are much more active hydrogenation catalysts, compared to Pt and Pd, which promote the undesired RWGS reaction. In the present study, the catalytic performance of Ru catalysts for the title reaction is investigated with respect to the loading and mean crystallite size of the metallic phase as well as with respect to the nature of the support (Al₂O₃, TiO₂, YSZ, CeO₂ and SiO₂). The aim is to identify key physicochemical parameters, which determine catalytic performance and to develop catalytic materials suitable for practical applications.

2. Experimental

Catalysts were prepared employing the wet impregnation method [21] with the use of Ru(NO)(NO₃)₃ (Alfa) as metal precursor salt and the following commercial metal oxide powders as supports: TiO₂ (Degussa P25), γ-Al₂O₃ (Alfa products), CeO₂ (Alfa products), SiO₂ (Alfa products) and YSZ (Tosoh 8Y-SZ). The resulting slurry was heated slowly to 70 °C under continuous stirring and maintained at that temperature until nearly all the water evaporated. The solid residue was dried at 110 °C for 24 h and then reduced at 400 °C in H₂ flow for 2 h. The nominal metal loading of catalysts thus prepared varied between 0.5 and 5 wt.%. In certain cases, where synthesis of catalysts with large Ru crystallites was desired, the dried samples were calcined in air at 600, 650 or 700 °C for a period of 2 or 4 h and then reduced with H₂ as described above.

Carriers and catalysts were characterized with respect to their specific surface area, exposed metallic surface area and mean crystallite size employing nitrogen physisorption at liquid nitrogen

temperature and selective chemisorption of H₂ (CO for Ru/CeO₂) at 100 °C. The mean crystallite size of the dispersed metal was estimated from hydrogen chemisorption data, assuming spherical particles, a H:Ru stoichiometry of 1:1, and an atomic surface area of Ru equal to 8.6 Å², using the relation:

$$d_M = \frac{6}{\rho_M S_M} \quad (4)$$

where d_M is the mean crystallite diameter, ρ_M is the density of Ru (12.3 g cm⁻³) and S_M is the exposed surface area per gram of metal. Details on the equipment and procedures used for catalyst characterization can be found elsewhere [33].

Catalytic performance tests and kinetic measurements have been carried out using an apparatus, which consists of a flow measuring and control system, the reactor and an on-line analysis system [21]. The flow system is equipped with a set of mass-flow controllers (MKS) and a set of valves, which allows introduction of the gas mixture to the reactor or to a by-pass loop, through stainless steel tubing. When desired, water is introduced to the system with the use of an HPLC pump (Marathon Scientific Systems), vaporized in a stainless steel evaporator maintained at 170 °C and mixed with the gas stream coming from the mass-flow controllers. The resulting gas mixture is then fed to the reactor through stainless steel tubing maintained at 150 °C by means of heating tapes. The reactor consists of a 40-cm long quartz tube (6 mm OD) with an expanded 1-cm long section in the middle (8 mm ID), in which the catalyst sample is placed. Reaction temperature is measured in the middle of the catalyst bed by means of a K-type thermocouple placed within a quartz capillary well, which runs through the cell. The reactor is placed in an electric furnace, the temperature of which is controlled using a second K-type thermocouple placed between the reactor and the walls of the furnace. A pressure indicator is used to measure the pressure drop in the catalyst bed. The analysis system consists of a gas chromatograph (Shimadzu) equipped with two packed columns (Porapak-Q, Carboxen) and two detectors (TCD, FID) and operates with He as the carrier gas. The response factors of the detectors were determined with the use of gas streams of known composition (Scott specialty gas mixtures). Reaction gases (He, 15%CO/He, CO₂, H₂) are supplied from high-pressure gas cylinders (Messer Griesheim GMBH) and are of ultra-high purity.

The catalytic performance of the prepared samples for the selective methanation of CO has been investigated in the temperature range of 170–470 °C using a feed stream consisting of 1%CO, 15%CO₂ and 50%H₂ (balance He). When water was added in the feed, part of the balance gas (He) was replaced by water vapor (10–30% H₂O). The mass of catalyst used in these experiments was typically 150 mg (particle size: 0.18 < d < 0.25 mm) and the total flow rate was 200 cm³/min. Prior to each experiment the catalyst sample was reduced *in situ* at 300 °C for 1 h under hydrogen flow (60 cm³ min⁻¹), purged with He, and then conditioned at 170 °C for 1 h with the reaction mixture. Conversions of reactants and selectivities toward products were then measured at that temperature using the analysis system described above. Selectivity to hydrogenation product “i” was calculated using the following expression:

$$S_i = \frac{C_{i,\text{out}}/\nu_i}{\sum_i C_{i,\text{out}}/\nu_i} \quad (5)$$

where ν_i is the number of carbon atoms of product “i”. Similar measurements were obtained following a stepwise increase of temperature up to ca. 470 °C. A few more measurements were then obtained by stepwise decreasing temperature to check for possible catalyst deactivation. It should be noted that the system was left at

Table 1

Physicochemical characteristics of synthesized catalysts and representative results of kinetic measurements.

Catalyst	Nominal Ru loading (wt.%)	Ru dispersion (%)	Mean Ru crystallite size (nm)	CO conversion		CO ₂ conversion	
				Rate at 215 °C (μmol s ⁻¹ g ⁻¹)	E _a (kcal mol ⁻¹)	Rate at 330 °C (μmol s ⁻¹ g ⁻¹)	E _a (kcal mol ⁻¹)
Ru/Al ₂ O ₃	0.5	70	1.3	0.10	18.4	1.90	38.8
	1.0	68	1.4	0.20	20.2	13.2	47.3
	2.0	63	1.5	0.56	21.0	11.7	36.2
	5.0	43	2.2	1.28	17.4	110.7	44.2
Calcined at:							
600 °C (2 h)	5.0	13	7.4	0.50	20.0	89.4	53.7
650 °C (4 h)	5.0	10	9.4	0.45	16.0	30.5	43.2
700 °C (4 h)	5.0	7	13.6	0.35	20.2	32.9	46.9
Ru/TiO ₂	0.5	46	2.1	0.08	23.2	0.54	42.6
	1.0	40	2.4	0.34	21.8	0.74	29.9
	2.0	29	3.2	1.89	29.9	21.3	32.3
	5.0	21	4.5	13.3	37.7	64.8	26.1
Ru/YSZ	5.0	33	2.9	0.34	28.7	42.4	30.6
Ru/CeO ₂	5.0	19	5.1	0.55	18.9	5.21	46.0
Ru/SiO ₂	5.0	17	5.5	0.13	29.4	27.0	22.4

each temperature for about 1 h under isothermal conditions in order to achieve steady state conditions. In all cases, data points are averages of at least three measurements. All experiments were performed at near atmospheric pressure.

Measurements of intrinsic rates were obtained in separate experiments where the conversions of reactants were kept below 10% so that differential reaction conditions could be assumed, with negligible heat and mass transfer effects. Results obtained, along with measurements of metal dispersion, were used to determine the turnover frequencies (TOFs) of carbon monoxide and carbon dioxide, defined as moles of CO or CO₂ converted per surface Ru atom per second. Details of the methods and procedures employed can be found elsewhere [21].

3. Results and discussion

3.1. Catalyst characterization

Specific surface areas of commercial metal oxide supports used in the present study were measured with the BET method and found to be 83 m²/g for Al₂O₃, 42 m²/g for TiO₂, 12 m²/g for YSZ, 3.3 m²/g for CeO₂ and 144 m²/g for SiO₂. The physicochemical characteristics of synthesized catalysts are summarized in Table 1, where Ru loading, dispersion and mean crystallite size (d_{Ru}) are listed for all samples investigated.

3.2. Effects of metal loading and crystallite size on catalytic performance

The effects of metal loading on catalytic activity and selectivity have been investigated over catalysts with variable Ru content (0.5–5 wt.%) supported on Al₂O₃ or TiO₂. Results obtained for Al₂O₃-supported samples are shown in Fig. 1A, where conversions of CO (X_{CO}) and CO₂ (X_{CO_2}) are plotted as functions of reaction temperature. It is observed that X_{CO} over the 0.5%Ru/Al₂O₃ catalyst increases with increasing temperature above 225 °C and goes through a maximum of ca. 50% at 320 °C. Further increase of temperature results in a drastic decrease of X_{CO} , which takes “negative” values above 360 °C. As has been discussed in our previous study [21], this behaviour can be explained by considering that, under the present conditions, CO hydrogenation (Eq. (1)) runs in parallel with the RWGS reaction (Eq. (3)), which becomes

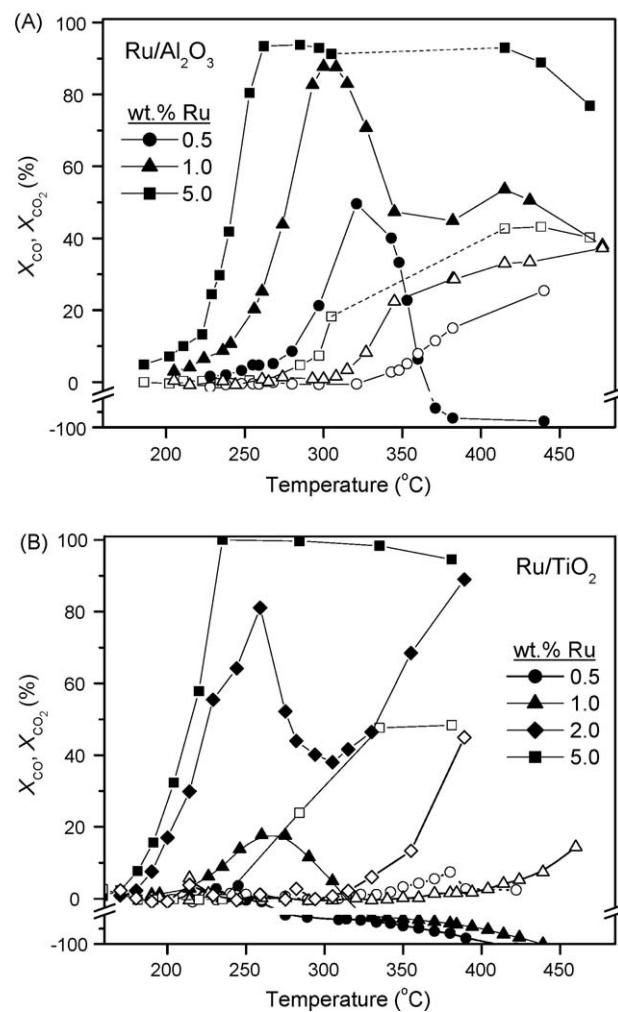


Fig. 1. Effect of metal loading on the catalytic performance of Ru catalysts supported on (A) Al₂O₃ and (B) TiO₂. Solid symbols: CO conversion; open symbols: CO₂ conversion. Experimental conditions—mass of catalyst: 150 mg; particle diameter: 0.18 < d_p < 0.25 mm; feed composition: 1%CO, 15% CO₂, 50% H₂ (balance He); total flow rate: 200 cm³/min.

important above ca. 320 °C. At temperatures higher than 360 °C the rate of CO production via the RWGS is higher than the rate of CO consumption via the methanation reaction, thereby resulting in the observed net increase of CO concentration at the effluent of the reactor. Regarding conversion of CO₂, it is practically zero at temperatures up to ca. 320 °C, i.e., until X_{CO} reaches its maximum value, and then progressively increases with increasing temperature (Fig. 1A). This behaviour, which is typical for all Ru catalysts investigated here as well as for Rh, Pt and Pd catalysts investigated in our previous study [21], reflects the fact that CO interacts more strongly with the catalyst surface, compared to CO₂.

Increasing Ru loading from 0.5 to 5 wt.% results in a progressive and significant shift of CO conversion curve toward lower temperatures (Fig. 1A). Note that X_{CO} and X_{CO₂} curves obtained for the 2%Ru catalyst (not shown for clarity) fall between those of 1%Ru and 5%Ru. The shift of CO-conversion curve is accompanied by an enhancement of X_{CO} maximum, which increases from 50% (at 320 °C) over the 0.5%Ru catalyst to 95% (at 260 °C) over the 5%Ru/Al₂O₃ catalyst. This implies that increasing Ru loading results in an increase of the relative rate of CO hydrogenation versus RWGS, especially in the lower temperature range. The CO₂-conversion curves also shift toward lower temperatures with increasing Ru loading in a manner, which is qualitatively similar to that observed for X_{CO} curves (Fig. 1A). It is of interest to note that under conditions where CO₂ methanation takes place, i.e., above ca. 300 °C, X_{CO} at a given temperature increases with increasing Ru content and does not take “negative” values for metal loadings higher than 1 wt.%. This indicates that CO₂ hydrogenation is strongly favored, compared to RWGS, with increasing Ru content.

The effect of metal loading on catalytic performance has been also studied with the use of Ru/TiO₂ catalysts, in order to investigate whether the beneficial effect of increasing Ru content on catalytic activity is also operable for oxide supports other than Al₂O₃. Results presented in Fig. 1B show that Ru/TiO₂ catalysts loaded with 0.5–1.0 wt.% Ru are practically inactive for CO/CO₂ methanation reactions and mainly catalyze the shift of CO₂ to CO. This is in accordance with results of our previous investigations, where it was shown that TiO₂-supported noble metal catalysts exhibit exceptionally high activity for the WGS reaction [33,34]. However, increasing Ru loading to 2 and 5% results in a significant increase of CO conversion, which is accompanied by a shift of X_{CO} curve toward lower temperatures (Fig. 1B). Interestingly, the 5%Ru/TiO₂ catalyst is able to completely and selectively hydrogenate CO at temperatures as low as 230 °C, whereas at higher temperatures CO₂ hydrogenation becomes significant. Thus, results obtained for both Al₂O₃- and TiO₂-supported catalysts show that hydrogenation of CO and CO₂ is strongly favored, compared to RWGS, with increasing Ru loading (Fig. 1).

It should be noted here that, in addition to methane, hydrogenation of CO/CO₂ mixtures under the present reaction conditions also results in the production of higher hydrocarbons. Typical results obtained over the 5%Ru/Al₂O₃ catalyst are shown in Fig. 2, where selectivities toward hydrogenation products (S_{C_xH_y}) are plotted as functions of reaction temperature. It is observed that S_{CH₄} increases from 75 to 100% with increasing temperature from 200 to 260 °C and does not further change at higher temperatures. The main by-products formed below 260 °C are C₂H₆, C₂H₄, C₃H₈ and C₃H₆, while with the onset of CO₂ methanation reaction, i.e., at temperatures above 260 °C (Fig. 1A), formation of higher hydrocarbons is diminished and the only hydrogenation product observed is CH₄ (Fig. 2). Qualitatively similar results were obtained for all catalyst samples investigated here.

The specific reaction rates of CO and CO₂ conversion under conditions of combined hydrogenation of CO/CO₂ mixtures have been measured for all Ru/Al₂O₃ and Ru/TiO₂ catalysts of variable

metal loading. Similar measurements have been also obtained for 5%Ru/Al₂O₃ catalysts calcined at 600–700 °C for 2–4 h in order to increase metal crystallite size. Typical results obtained at 215 °C (for CO conversion) and 330 °C (for CO₂ conversion) are listed in Table 1, along with the corresponding values of apparent activation energies estimated from Arrhenius-type diagrams. It is observed that the rate (per gram of catalyst) increases with increasing metal loading for both CO and CO₂ consumption. Interestingly, for certain sets of catalysts, this increase is significantly higher than that expected by only taking into account the presence of higher metal content. For example, increasing loading of Ru/TiO₂ catalysts by a factor of 10 (i.e., from 0.5 to 5 wt.%) results in an increase of the rate of CO conversion at 215 °C by a factor of 166 (i.e., from 0.08 to 13.3 μmol s⁻¹ g⁻¹) and of the rate of CO₂ conversion at 330 °C by a factor of 120 (i.e., from 0.54 to 64.8 μmol s⁻¹ g⁻¹) (Table 1). This behaviour implies that CO/CO₂ hydrogenation reactions are structure sensitive, i.e., that the intrinsic reaction rates depend on crystallite size of the dispersed metallic phase. This is clearly observed in the Arrhenius plots of Fig. 3, where it is shown that TOFs of CO and CO₂ over Ru/Al₂O₃ (Fig. 3A) and Ru/TiO₂ (Fig. 3B) increase by more than one order of magnitude with increasing Ru content or, equivalently, with increasing mean crystallite size.

The effect of mean Ru crystallite size (d_{Ru}) on catalytic activity is presented in Fig. 4, where the TOFs of CO at 215 °C (Fig. 4A) and CO₂ at 330 °C (Fig. 4B) are plotted as functions of d_{Ru} for all Al₂O₃- and TiO₂-supported catalysts investigated. It is observed that specific activity for both CO and CO₂ hydrogenation reactions is significantly improved with increasing metal crystallite size. In particular, TOFs of CO and CO₂ over Ru/TiO₂ catalysts increase by a factor of 40 (at 215 °C) and 25 (at 330 °C), respectively, with increasing Ru crystallite size from 2.1 to 4.5 nm. The effect is smaller for Ru supported on Al₂O₃, where TOFs of CO and CO₂ conversion increase by a factor of 3.5 (at 215 °C) and 17 (at 330 °C), respectively, with increasing d_{Ru} from 1.3 to 13.6 nm.

The structure sensitivity of dispersed noble metals for CO and CO₂ hydrogenation reactions has been reported by several authors, but results are often contradicting and seem to depend on the experimental conditions used (e.g. reaction temperature, solo-methanation of CO or CO₂ versus co-methanation of CO/CO₂ mixtures, etc.) and metal-support combination employed. For instance, Ojeda et al. [29,30] found that TOF of CO increases by a factor of 4 over Rh/Al₂O₃ catalysts with increasing metal particle

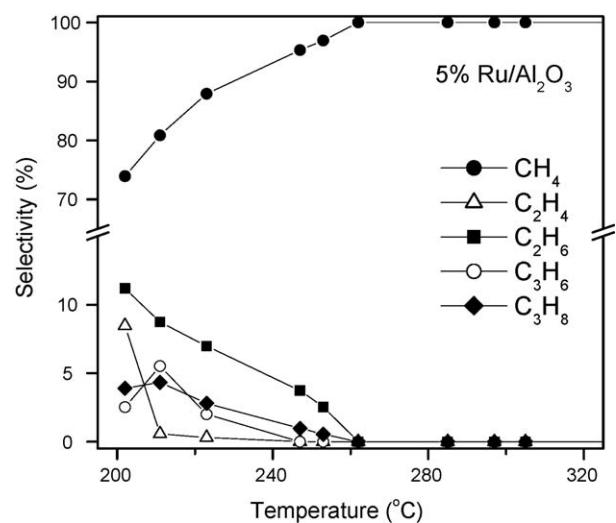


Fig. 2. Effect of reaction temperature on the selectivity of 5%Ru/Al₂O₃ catalyst to the hydrogenation products. Experimental conditions: same as in Fig. 1.

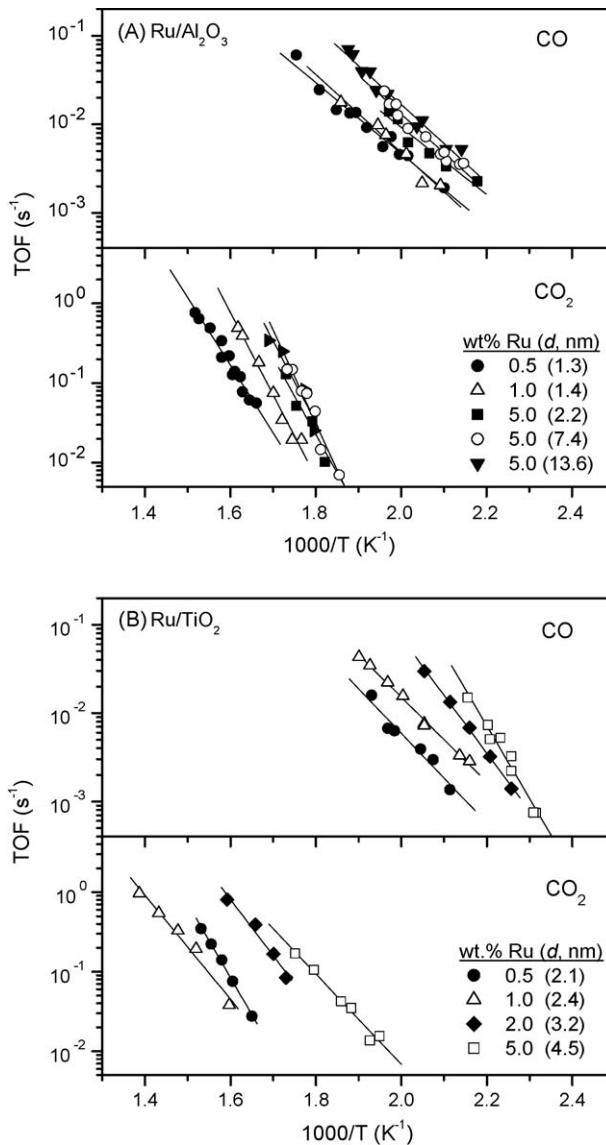


Fig. 3. Arrhenius plots of turnover frequencies of CO and CO_2 obtained over (A) Ru/ Al_2O_3 and (B) Ru/TiO₂ catalysts of variable metal loading and mean crystallite size under differential reaction conditions.

size from 5 to 30 nm. Hanaoka et al. [31] also demonstrated that CO hydrogenation to methanol and C₂-oxygenates is favored over Rh/SiO₂ catalysts with larger metal particles, while hydrogenation of ethylene is suppressed with increasing Rh particle size. Recently, Dagle et al. [9] reported that the performance of Ru/Al₂O₃ catalysts for the selective methanation of CO is markedly affected by Ru crystallite size, in the range of 7.5–34.2 nm, in a way similar to that observed in the present study. On the other hand, Wang et al. [26] concluded that methanation of CO over Pd/SiO₂ catalysts is structure insensitive, at least for Pd crystallites in the range of 3–30 nm. Regarding CO_2 methanation, it has been reported that activity of Ni/Al₂O₃ catalysts increases with increasing Ni content in the range of 5–25 wt%, but methane production per m² of nickel surface area is enhanced for samples with lower Ni loadings [32]. For combined methanation of CO/ CO_2 mixtures, Takenaka et al. [35] found that larger Ni crystallites and smaller Ru crystallites are more effective for CO methanation. The latter conclusion, which is opposite to the findings of the present study, is questionable because it compares specific activity of Ru catalysts dispersed on different supports. As will be shown below, the nature of the metal

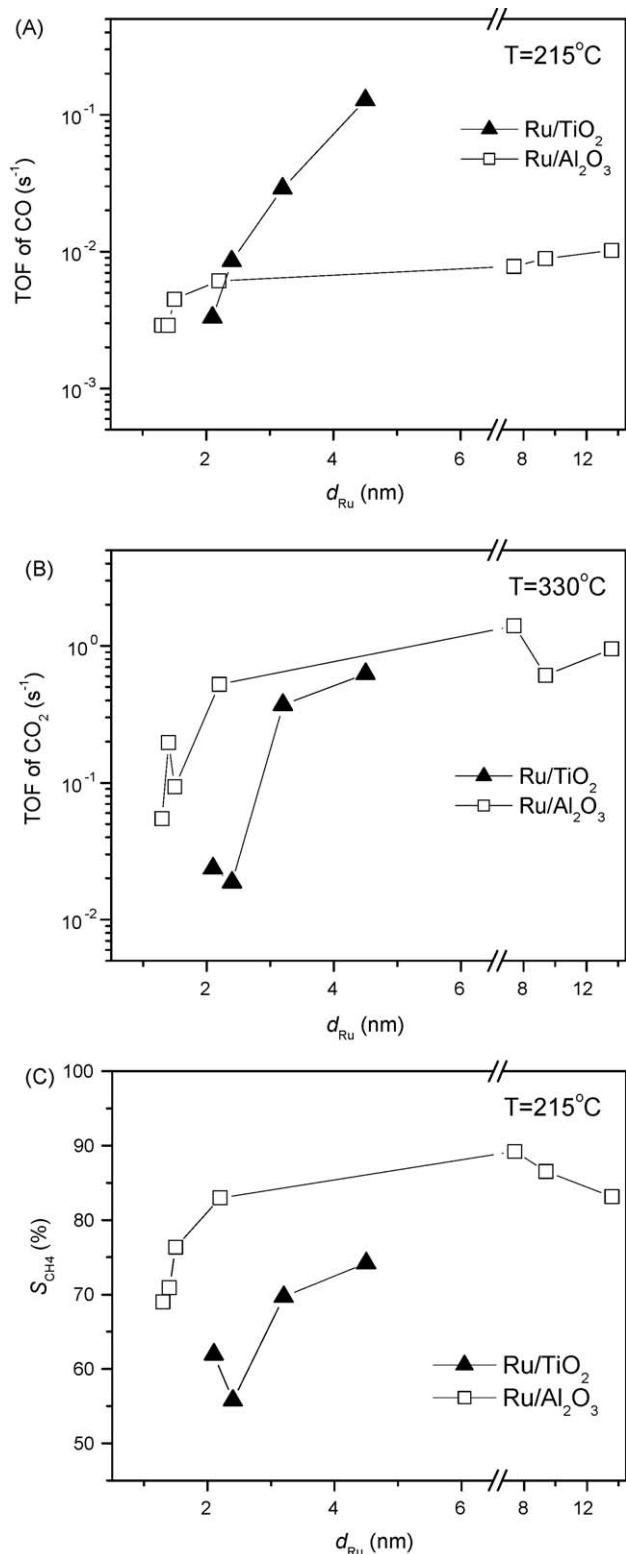


Fig. 4. Effects of mean Ru crystallite size (d_{Ru}) of Al₂O₃- and TiO₂-supported catalysts on (A) the turnover frequency of CO at 215 °C, (B) the turnover frequency of CO_2 at 330 °C and (C) the selectivity toward CH₄ at 215 °C. Experimental conditions: same as in Fig. 1.

oxide carrier affects considerably the activity of supported Ru crystallites.

Results presented in Fig. 4A and B may be explained by considering that the fraction of coordinatively unsaturated Ru

atoms at edges and corners relative to the total amount of surface metal atoms decreases with increasing crystallite size. The observed dependence of TOF from crystallite size (Fig. 4) indicates that hydrogenation of CO/CO₂ occurs preferably on flat Ru surfaces, the fraction of which is higher for larger metal crystallites. Since both CO and CO₂ hydrogenation reactions are believed to involve a CO dissociation step [22,36–39], this behaviour probably indicates that larger Ru particles facilitate the cleavage of the C–O bond. It is important to note here that results of our previous studies [33,34] showed that the rate of the WGS reaction over supported noble metal catalysts is structure insensitive, i.e., it does not depend on metal loading or crystallite size. Thus, the beneficial effect of increasing Ru loading on CO/CO₂ hydrogenation observed in Fig. 1 can be explained by considering that the rate of the hydrogenation reactions increases drastically with increase of Ru crystallite size whereas the rate of the RWGS reaction is not affected by varying this parameter.

Regarding the apparent activation energy of CO hydrogenation, results summarized in Table 1 show that it does not vary significantly with metal crystallite size for Ru/Al₂O₃ (16–20 kcal/mol) catalysts, whereas it increases substantially for Ru/TiO₂ catalysts with increasing d_{Ru} (22–38 kcal/mol). In the case of CO₂ hydrogenation, values of E_a scatter in relatively wide ranges, i.e., 36–53 kcal/mol for Ru/Al₂O₃ and 26–42 kcal/mol for Ru/TiO₂, but do not present any trend with respect to metal particle size (Table 1). This finding is in accordance with results of Wang et al. [26], who found that activation energy for CO hydrogenation over Pd/Al₂O₃ catalysts takes values in the range of 13.8–24.5 kcal/mol, with no trend consistent with Pd crystallite size (3–30 nm). Similar were the findings of Aksaylu et al. [32], who investigated the CO₂ methanation reaction over Ni/Al₂O₃ catalysts with variable Ni loading (5–25 wt.%). It may be suggested that the observed “random” variation of E_a with metal crystallite size reflects the fact that several reactions run simultaneously under the present conditions, including CO and CO₂ methanation, hydrogenation to higher hydrocarbons and RWGS reaction, each one of which depends in a different manner on temperature, nature of the support and metal crystallite size.

The mean particle size of Ru also affects selectivity toward hydrogenation products. Typical results obtained at 215 °C are shown in Fig. 4C, where S_{CH_4} is plotted as a function of d_{Ru} . It is observed that for Ru catalysts supported on TiO₂ or Al₂O₃, selectivity toward methane increases with increasing metal crystallite size. Effects of d_{Ru} on selectivity become less pronounced at higher temperatures, and S_{CH_4} becomes 100% with the onset of CO₂ methanation reaction for all catalyst samples investigated.

3.3. Influence of the nature of the support

The effect of the nature of the support on catalytic performance has been investigated over Ru catalysts of the same metal content (5 wt.%) supported on five different commercial metal oxide powders (TiO₂, Al₂O₃, YSZ, CeO₂ and SiO₂). Results obtained are summarized in Fig. 5A, where conversions of CO and CO₂ are plotted as functions of reaction temperature. It is observed that Ru/TiO₂ exhibits a superior performance, compared to Ru/Al₂O₃, Ru/CeO₂ and Ru/YSZ catalysts, whereas Ru/SiO₂ is practically inactive for selective methanation of CO and only promotes the RWGS reaction. It may be noted here that the decrease of CO conversion observed above 400 °C (Fig. 5A) may be attributed to thermodynamic limitations, because ΔG of CO methanation reaction increases with increasing temperature and becomes positive at temperatures higher than 530 °C [40].

Results of kinetic measurements (Fig. 5B) show that the specific reaction rate of CO conversion depends strongly on the nature of the support. In particular, activity decreases in the order of TiO₂ > Al₂O₃, CeO₂ > YSZ > SiO₂ with TOF at 200 °C being ca. two orders of magnitude higher when Ru is supported on TiO₂, compared to SiO₂. It should be noted, however, that the crystallite size of Ru varies in the range of 2.2–5.5 nm for this set of catalysts (Table 1) and, therefore, the observed catalyst ranking may be somewhat different for Ru catalysts of the same crystallite size. Regarding CO₂ conversion, differences in catalytic activity are less pronounced, with Ru/TiO₂ being the most active catalyst among samples of this series (Fig. 5B).

Selectivity to CH₄ at a given temperature does not depend appreciably on the nature of the support (Fig. 6). In all cases, S_{CH_4} increases from 60 to 70% at ca. 200 °C to 100% at ca. 300 °C and remains at this level upon further increasing temperature.

The apparent activation energies of CO and CO₂ hydrogenation reactions depend on the nature of the support and vary in the ranges of 17–38 kcal/mol and 22–46 kcal/mol, respectively (Table 1). A similar effect of the support on E_a has been reported

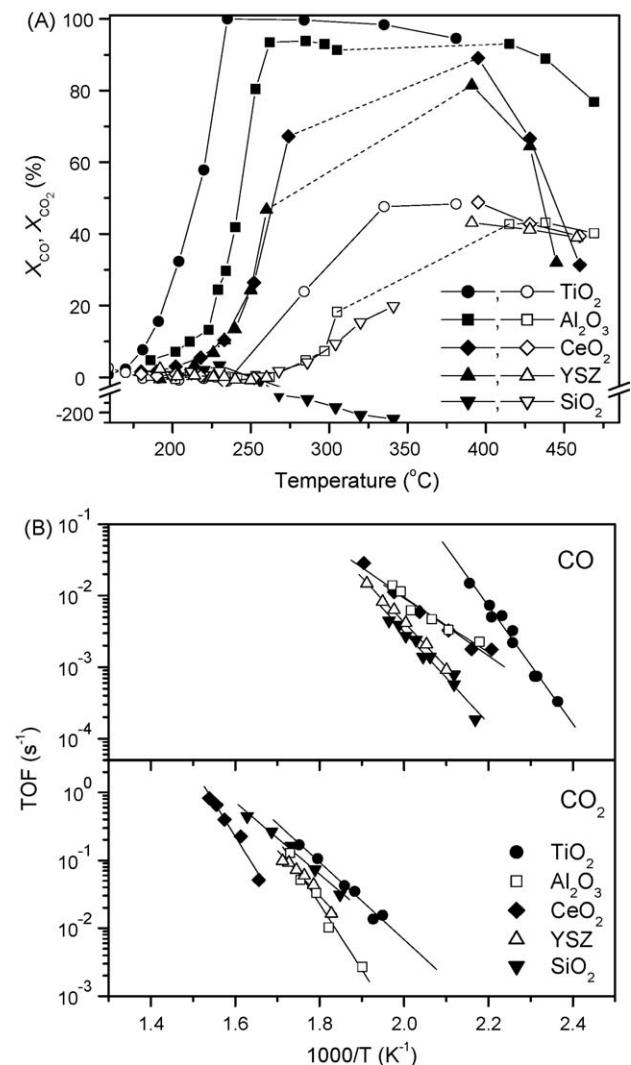


Fig. 5. (A) Catalytic performance of Ru (5 wt.%) supported on the indicated commercial oxide carriers. Solid symbols: CO conversion; open symbols: CO₂ conversion. (B) Arrhenius plots of turnover frequencies of CO and CO₂ obtained over the same catalysts under differential reaction conditions. Feed composition: same as in Fig. 1.

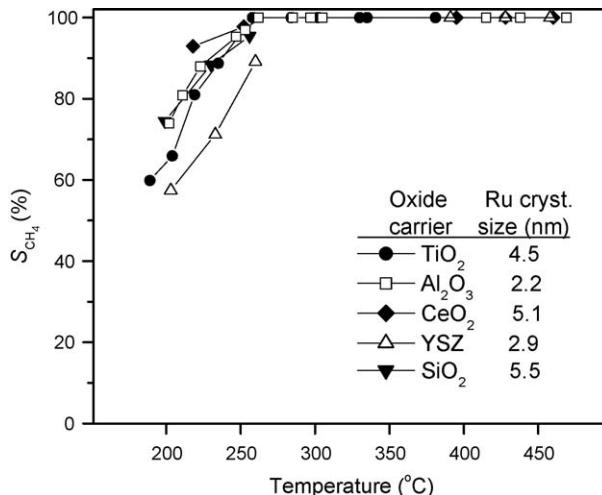


Fig. 6. Effect of the nature of the support on the selectivity of Ru (5 wt.%) catalysts to methane. Data were obtained from Fig. 5A.

by Wang et al. [26], who found that the activation energy for the CO hydrogenation reaction over Pd catalysts supported on Al₂O₃, TiO₂ and SiO₂ depends on the nature of the support taking values of 13.8, 19.7 and 27.7 kcal/mol, respectively.

Results presented in Fig. 5 and Table 1 clearly show that catalytic activity of Ru and apparent activation energy of CO/CO₂ hydrogenation reactions depend strongly on the nature of the support, with Ru/TiO₂ exhibiting the best performance for the title reaction. The beneficial effect of TiO₂ support for CO methanation has been reported by several authors. For Pd catalysts, it has been found that activity is significantly higher when Al₂O₃, ZrO₂, La₂O₃, or Nd₂O₃ are used as supports, than when SiO₂ is used or when Pd is used in an unsupported form ([27] and refs. therein). Wang et al. [26] reported that specific activity of Pd increases by more than two orders of magnitude depending on the nature of the support in the order of Pd/SiO₂ < Pd/SiO₂–Al₂O₃ ≈ Pd/Al₂O₃ < Pd/TiO₂. This strong effect has been attributed to interaction between the Pd crystallites and the support. Erdöhelyi et al. [28] reported that the rate of CH₄ formation on the most active Pd/TiO₂ catalyst was two orders of magnitude higher than that of the less active Pd/MgO sample. The same group also found that Pd/TiO₂ catalyst exhibits superior catalytic performance for methanation of CO₂ [28]. These authors proposed that the rate-determining step for both CO and CO₂ methanation reactions is the dissociation of adsorbed CO, which is favored over Pd/TiO₂ catalyst, due to electronic interactions between TiO₂ and Pd. These interactions are smaller over Pd/Al₂O₃ and do not exist at all for Pd/MgO and Pd/SiO₂ samples. Similar were the conclusions obtained over supported Rh catalysts [22,41].

Regarding product selectivity, Shen et al. [42] demonstrated that reaction of CO with H₂ over Pd/Al₂O₃ leads to the production of dimethyl ether, Pd/SiO₂ and Pd/ZrO₂ favor the formation of methanol, while only Pd/TiO₂ catalyst yields CH₄ as the main product. The higher methane selectivity of Pd/TiO₂ was assigned to the decoration effect of the reduced TiO_x species on Pd surface, which aids the dissociation of CO. In contrast, Bracey and Burch [27] concluded that the SMSI cannot be used to interpret the high activity of TiO₂-supported catalysts. They proposed that the effect of TiO₂ and other supports on catalytic activity is due to the formation of new active sites in the surface of the support, adjacent to a normal metal particle. These sites should be capable of adsorbing and dissociating CO, thereby enhancing the rate of CO hydrogenation. This is in general agreement with results of our recent work on the WGS reaction [43,44], where it was proposed

that the enhanced activity of platinum catalysts supported on reducible metal oxides, especially TiO₂ and CeO₂, is due to the creation of new active sites with exceptional electron donating properties, located at the metal–support interface. Clearly, a final conclusion on the role of the support on the catalytic performance of noble metals for the title reaction requires a detailed investigation of the reaction mechanism, which is beyond the scope of the present study.

3.4. Effects of space velocity

Results presented in Figs. 1–6 were obtained with a relatively high space velocity (SV) of ca. 48,800 h⁻¹. In order to investigate the effect of SV on catalytic performance, experiments were conducted by varying this parameter in the range of 12,200–48,800 h⁻¹. Typical results obtained over the 0.5%Ru/Al₂O₃ catalyst are summarized in Fig. 7. It is observed that the conversion curve of CO is progressively shifted toward lower temperatures with decreasing space velocity from 48,800 to 12,200 h⁻¹ (Fig. 7A). This is accompanied by an increase of X_{CO} maximum from 50% (at 320 °C) to 97% (at 280 °C). It is of interest to note that the effect of decreasing SV is qualitatively similar to that observed with increasing Ru loading from 0.5 to 5% (Fig. 1). The conversion curve

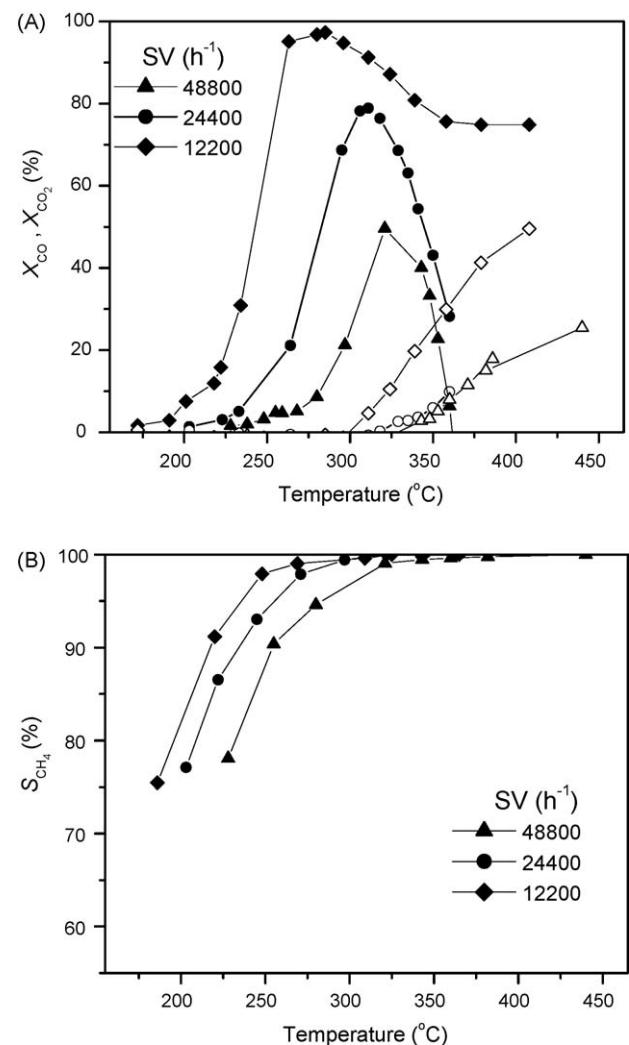


Fig. 7. Effect of space velocity on the catalytic performance of 0.5%Ru/Al₂O₃ catalyst. (A) Conversions of CO (solid symbols) and CO₂ (open symbols); (B) selectivity to methane.

of CO_2 also shifts toward lower temperatures with decreasing space velocity, but differences in X_{CO_2} are less important, compared to those of X_{CO} (Fig. 7A). Results obtained from similar experiments over the 5%Ru/Al₂O₃ and 5%Ru/TiO₂ catalysts (not shown for brevity) did not show drastic differences in catalytic performance upon varying space velocity. In particular, decreasing SV from 48,800 h⁻¹ to 24,400 h⁻¹ resulted in a shift of the X_{CO} curves toward lower temperatures by ca. 20 °C, whereas the X_{CO_2} curve was practically not affected.

In addition to the observed increase of X_{CO} , decrease of space velocity also results in an increase of selectivity to CH_4 (Fig. 7B). As a general observation, S_{CH_4} always increases with increasing X_{CO} in a manner which does not depend on whether this is due to an increase of reaction temperature (Fig. 2), to the effect of metal crystallite size (Fig. 4C), to the effect of the oxide support (Fig. 6) or to variations of space velocity (Fig. 7B). CO methanation always proceeds with a parallel production of higher hydrocarbons, the concentration of which drops close to zero with the onset of CO_2 methanation. Inui et al. [45] showed that the presence of carbon species on the catalyst surface, which is believed to be related to the formation of higher hydrocarbons, has a strong retarding effect on CO methanation, which is released with increase of CO conversion. In contrast, the presence of surface carbon species in CO_2 methanation has been reported to be negligible, compared to CO hydrogenation [45]. Similar conclusions were obtained over supported Rh catalysts, where the lifetime and the surface population of higher hydrocarbons were found to be considerably lower in CO_2 hydrogenation, compared to CO hydrogenation [22].

3.5. Effects of water vapor

The reformate gas produced in fuel reformers contains considerable amounts of water steam, which may influence CO removal via selective methanation. In order to investigate this issue, the effect of the presence of water vapor in the feed on catalytic performance has been investigated over the most active 5%Ru/TiO₂ catalyst and results obtained are shown in Fig. 8. It is observed that the conversion curve of CO remains practically unaffected by the presence of water, while the conversion curve of CO_2 is shifted toward higher temperatures with increasing water content from 0 to 30%. This behaviour may be of significant practical importance, because the temperature window between the maximum CO conversion and the onset of CO_2 methanation becomes wider in the presence of steam, thereby making it easier to select and optimize operating conditions for preferential methanation of CO under realistic reaction conditions. This finding is in accordance with results of our previous study where it was shown that solo-methanation of CO_2 is retarded in the presence of water over noble metal catalysts supported on Al₂O₃ [21], and those of Batista et al. [46], who reported that the CO_2 methanation does not occur appreciably in the presence of water in the feed.

The observed dependence of CO and CO_2 conversions on water vapor concentration can be understood by considering the mechanism of CO/ CO_2 hydrogenation reactions. It has been proposed that CO methanation proceeds via dissociation of carbon monoxide to C and O atoms, followed by their hydrogenation into CH_4 and H_2O [1,29–32]. Results of Fig. 8 show that this reaction is not affected appreciably by the presence of water. Regarding CO_2 methanation, it is believed to involve conversion of CO_2 toward CO via the RWGS (Eq. (3)), followed by CO hydrogenation to methane [1]. If this is the case, then increase of water concentration in the feed should shift Eq. (3) to the left, thereby resulting in a decrease of CO_2 conversion in agreement with results of Fig. 8.

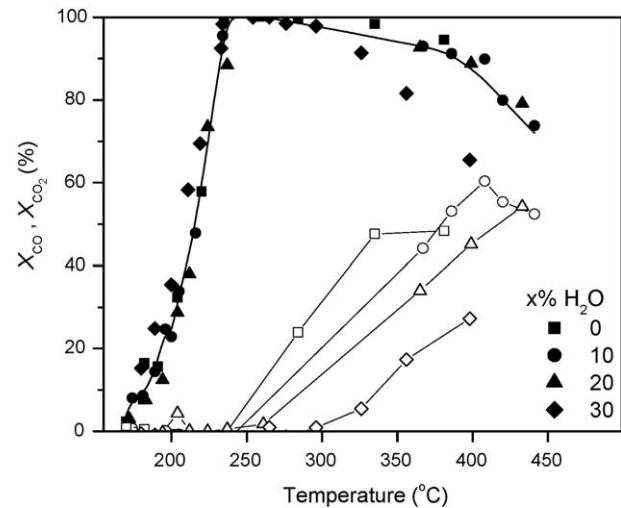


Fig. 8. Effect of addition of water vapor in the feed (0–30%) on the catalytic performance of 5%Ru/TiO₂ catalyst for the selective methanation of CO. Solid symbols: CO conversion; open symbols: CO_2 conversion.

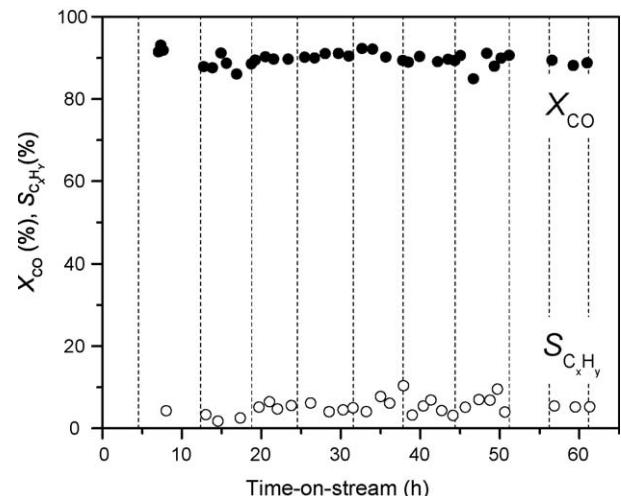


Fig. 9. Long-term stability test of the 5%Ru/TiO₂ catalyst: Alterations of the conversion of CO and selectivities toward higher hydrocarbons (C_xH_y) with time-on-stream. Feed composition: 0.5%CO, 14% CO_2 , 55.5% H_2 , 30% H_2O ; $T = 230^\circ\text{C}$; $\text{SV} = 48,800 \text{ h}^{-1}$.

3.6. Long-term stability test of 5%Ru/TiO₂ catalyst

The long-term stability of 5%Ru/TiO₂ has been investigated with the use of a realistic feed composition consisting of 0.5%CO, 14% CO_2 , 55.5% H_2 and 30% H_2O . The space velocity (48,800 h⁻¹) and reaction temperature (230 °C) employed were chosen so as to keep conversion of CO below 100%. Results obtained are presented in Fig. 9, where X_{CO} and $S_{\text{C}_x\text{H}_y}$ are plotted as functions of time-on-stream. Dashed vertical lines indicate shutting down of the system overnight, where the catalyst was kept at room temperature under He flow. It is observed that 5%Ru/TiO₂ exhibits excellent stability for more than 60 h-on-stream, with conversion of CO being about 90% and selectivity to higher hydrocarbons around 5%. Conversion of CO_2 (not shown for clarity) is also stable taking values below 2%.

4. Conclusions

Results of the present study show that supported Ru catalysts are capable of completely and selectively methanate CO in the

presence of excess CO₂, provided that catalyst characteristics are optimized and operating conditions are properly selected. Generally, hydrogenation of CO is the predominant reaction until a certain temperature is reached, above which conversion of CO starts to decrease due to the onset of the RWGS reaction and hydrogen starts to be unselectively consumed to methanate CO₂. Catalytic performance for the title reaction is greatly enhanced with increase of Ru loading and depends strongly on the nature of the oxide support employed. Activity for CO/CO₂ hydrogenation is significantly improved when Ru is supported on TiO₂, compared to Al₂O₃, CeO₂, YSZ or SiO₂. Both hydrogenation reactions are structure sensitive, and specific activity (TOF) increases by more than one order of magnitude with increasing Ru crystallite size. Conversion curves of CO are shifted toward lower temperatures with increasing metal loading and/or with decreasing space velocity, which is accompanied by an increase of selectivity toward methane. Selectivity to methane generally increases with increasing conversion of CO in a manner, which does not depend on whether this is due to an increase of reaction temperature, to the effect of metal crystallite size, to the effect of the oxide support or to variations of space velocity. Among the various noble metal-support combinations investigated, optimal results were obtained over the 5%Ru/TiO₂ catalyst, which is able to completely and selectively methanate CO at temperatures around 230 °C. Addition of up to 30% water vapor in the feed does not practically affect conversion of CO over this catalyst but retards CO₂ methanation, thereby expanding the temperature window of operation for the title reaction. Long-term stability tests showed that the 5%Ru/TiO₂ catalyst is very active, selective and stable under realistic reaction conditions and, therefore, is a promising candidate for use in the selective methanation of CO for fuel cell applications.

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